SEPARATION AND DETERMINATION OF LINEAR AND BRANCHED CHAIN ALKYLBENZENE SULFONATES BY SALTING-OUT CHROMATOGRAPHY

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SUMMARY

The separation and determination of biologically "soft" (LAS) and "hard" (ABS) alkylbenzene sulfonates in blends of the two was investigated by salting-out chromatography. The analytical conditions were as follows: column, 26 mm I.D. and 500 mm long; resin, Amberlite CG-50 (100–200 mesh); developing solution, 0.5 M ammonium sulfate–43% methanol solution; and column temperature, 50°.

Quantitative separation of LAS and ABS was satisfactory and the peak resolution between them more than unity.

INTRODUCTION

There are two types of biologically "soft" (LAS) and "hard" type (ABS) alkylbenzene sulfonates used as raw materials for household synthetic detergents. Actually a mixture of the two types is in everyday use in our country although the conversion from the hard to the soft type can be carried out in the same way as in other countries.

Thus, it would be worth while establishing a rapid and precise analytical method for both types of sulfonate mixture. Many methods have been studied for the analysis of mixtures of LAS and ABS.

The JIS (Japanese Industrial Standard)[1] method is based on the measurement of biological degradation and takes a long analysis time. In IR methods[2-6], the extent to which the LAS to ABS ratio can be determined is limited, because the overlap of the absorption LAS and ABS bands makes the quantitative analysis of a mixture difficult when one sulfonate is present in a much higher concentration than the other. NMR[7-9] and GC[10-13] methods necessitate desulfonation of the sulfonate mixture.

ROSEN AND GOLDSMITH[14] have investigated extensively the separation and determination of mixtures of ionic and nonionic surface active agents by ion-exchange chromatography. However, there have been no reports on the separation and determination of mixtures of several ionic surface active agents.

On the other hand, SARGENT AND RIEMAN[15] succeeded in separating for the first time a mixture of nonelectrolytic organic compounds by salting-out chromato-

graphy using an ion-exchange resin. FUNASAKA and co-workers[16,17] satisfactorily applied this technique to the analysis of organic sulfonic isomers (*e.g.* dyestuff intermediates).

The present paper describes the separation and the determination of LAS and ABS mixtures by a salting-out chromatography technique.

EXPERIMENTAL

Apparatus

The distribution coefficient was measured by a batch method using a 50 ml conical flask with a stopper. A shaker (Model KM, Iwaki Co., Ltd.) was employed to obtain the adsorption equilibrium rapidly. Absorbance of the material separated was measured by a spectrophotometer (Model QV-50, Shimadzu Co., Ltd.) with a quartz cell (cell thickness 2 cm). The glass column (26 mm I.D. and 500 mm long) was equipped with a jacket in order to control the column temperature.

The temperature of the circulating water was controlled by a constant temperature water circulation unit (Model 1, Shimadzu Co., Ltd.). A Uvicord II detector (LKB-Produkter AB Co., Ltd., Sweden; wavelength 254 mμ) was employed for automatically recording the elution chromatogram. The polyethylene tube (1.8 mm outside diameter) was used to connect the column to the Uvicord II detector. After passing through the Uvicord II detector, the eluate was directed to the fraction collector (model SF-160K, Toyo-Kagaku Co., Ltd.) where it was collected in a volumetric flask.

Reagents and samples

Amberlite CG-50 (100–200 mesh), a weakly acidic cation-exchange resin, was used as a column substrate. The methanol in the eluent was weighed in order to make the eluent composition precise.

The LAS and ABS were manufactured by our company and purified by the following procedure. 3 g of sample was dissolved in 250 ml of 50% of aqueous ethanol solution and extracted three times with 100 ml of petroleum ether to remove unreacted substances. The aqueous ethanol solution was evaporated to dryness and then the sample was redissolved in ethanol. The ethanol solution was filtered to remove sodium chloride and the filtrate was dried on the waterbath.

A standard sample solution was prepared by dissolving a purified sulfonate in water. It was titrated with 0.01 *M* cetylpyridinium chloride solution using Methylene Blue as indicator.

Procedure

Measurement of distribution coefficient. In order to find suitable column conditions, the distribution coefficients of LAS and ABS with the resin were first measured by a batch method. The ion-exchange resin was washed with ethanol using a Soxhlet extractor, treated with 3 *N* sodium hydroxide and 3 *N* aqueous hydrogen chloride solution alternately, then washed thoroughly with water and finally dried at 105° for 5 h. About 1 g of this dried resin was weighed out accurately and put into a 50 ml stoppered conical flask. 25 ml of each salting-out reagent solution, of various concentrations, was added to each flask containing 1 g of resin. The flasks were allowed to

stand for 1 h in order to swell the resin. 1 ml of sample solution containing LAS and ABS (1 ml of solution contains 10 mg of sample) was added to each respective flask, which was shaken vigorously for 20 min at intervals of 1 h during first 3 h, then allowed to stand for 15 h in order to obtain adsorption equilibrium. The resin was filtered off and absorbances of the filtrates were measured against a blank solution.

The distribution coefficient K_d was calculated from the following equation:

$$K_d = \frac{\text{amount of sample adsorbed on 1 g of resin (mg/g)}}{\text{amount of sample contained in 1 ml of solution (mg/ml)}}$$

The maximum adsorption wavelength of both LAS and ABS in the UV region was 261 mμ.

Salting-out chromatography. The salting-out chromatographic procedure was performed as follows. The resin was poured into the column by the wet method, after which the resin bed in the column was settled by passing the eluent (0.5 M ammonium sulfate–43% methanol solution) through it for 1 h. For column temperatures higher than room temperature, the eluent solution with the resin suspended in it was heated a little higher than the column temperature before being poured into the column.

1 ml of sample solution was adsorbed carefully on the top of the resin bed, then the inside wall of the column was washed several times with the same eluent.

The flow rate was controlled by a stopcock, the eluate was passed through the Uvicord II detector and the elution chromatogram recorded.

Quantitative analysis, *i.e.* an operation to calculate the recovery of a sample, was carried out according to the following method. The chromatogram recorded by the Uvicord II detector was used as a monitor, the eluate of a section showing an elution peak was collected in a volumetric flask, and diluted with eluent to volume. A reference solution was prepared by diluting 1 ml of sample solution to the same volume. The absorbance of both solutions was measured at 261 mμ using eluent as the blank solution; recovery was calculated from the absorbance ratio of the sample solution against the reference solution.

Substances which were not eluted with this eluent were eluted with 43% aqueous methanol solution containing no salting-out reagent. The column could be used again to analyze the next sample.

RESULTS AND DISCUSSION

Salting-out reagent and distribution coefficient

Four kinds of salting-out reagents (sodium chloride, ammonium sulfate, am-

TABLE I

EFFECT OF SALTING-OUT REAGENTS ON DISTRIBUTION COEFFICIENTS OF LAS AND ABS

Reagent	Distribution coefficient (ml/g)		Ratio K_{d_1}/K_{d_2}
	K_{d_1}(LAS)	K_{d_2}(ABS)	
NaCl	152	104	1.46
NH$_4$NO$_3$	214	101	2.12
(NH$_4$)$_2$SO$_4$	256	104	2.46
CaCl$_2$	—	—	

monium nitrate and calcium chloride) were tested for their effect on the distribution coefficients of LAS and ABS, by a batch method.

Table I shows the distribution coefficients where the concentration of each salting-out reagent was 0.05 M.

With calcium chloride, a measurement was impossible on account of the formation of white turbidity due to the strong salting-out action.

Eluent

In the separation of both sulfonates by the column method, it is desirable that the distribution coefficient ratio is greater than 1.5, and, furthermore, that the distribution coefficients are less than 100.

FUNASAKA and his co-workers[17] reported that the amount of adsorption decreased when alcohol was present in the salting-out reagent solution.

Thus, a salt–methanol solution system was investigated. At first, the effect of the concentration of the salting-out reagent and the methanol on the distribution coefficient was investigated for a sodium chloride–methanol system. In the experimental range in which the elution is possible, the distribution coefficient ratio of LAS and ABS was small. As a result of this the system was unsatisfactory as a developing solvent. Ammonium sulfate–methanol mixtures were next investigated, because the distribution coefficient ratio was larger than in the case of sodium chloride. The results
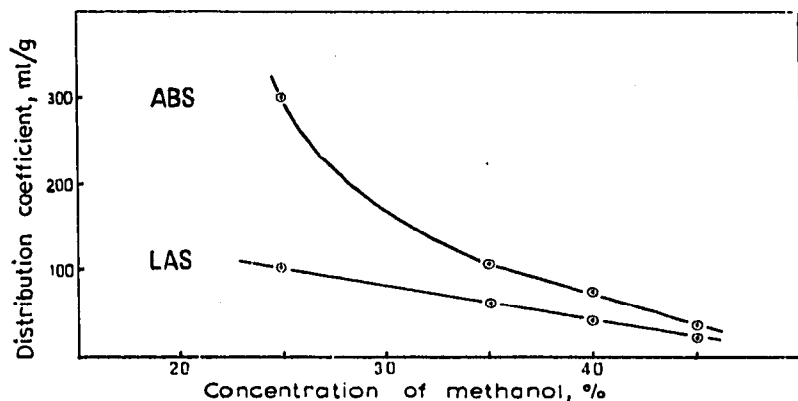

Fig. 1. Effect of the concentration of methanol on the distribution coefficients of LAS and ABS. Concentration of ammonium sulfate solution was 0.5 M.

are presented in Fig. 1, which shows that the larger the concentration of methanol, the lower the distribution coefficient. It seems that the molecules of alcohol tend to accumulate on the surface of the resin, thus preventing the sample being adsorbed on the resin and that the solubility of the surface active agent is greater in alcohol solution than in water. It is thought that the distribution coefficient is lowered by these two factors. A mixture of 0.5 M ammonium sulfate and 43% of methanol solution was selected as the eluent from the results presented in Fig. 1.

Column temperature

The effects of the column temperature on the separation and recovery of LAS and ABS mixtures were investigated. The preparation was carried out at 40°, 45° and 50° under constant conditions except for the column temperature.

TABLE II

EFFECT OF COLUMN TEMPERATURE ON RECOVERIES OF LAS AND ABS

Sample taken: LAS 8.70 mg; ABS 9.20 mg.

Column temp. (°C)	Recovery (%)	
	LAS	ABS
50	98.9	100.1
45	84.5	97.1
40	76.0	93.0

When the column temperature was 40° or 45°, the recoveries of both sulfonates were lower than 100% as shown in Table II. Table II shows that the higher the column temperature the more suitable were the column conditions. The column temperature was fixed at 50°, taking into account the use of methanol in the eluent and the difficulty of the operation.

Separation by the column method

The separation of LAS and ABS was carried out under the following conditions: eluent, 0.5 M ammonium sulfonate–43% methanol solution; column size, 500 × 26 mm I.D.; column temperature, 50°.

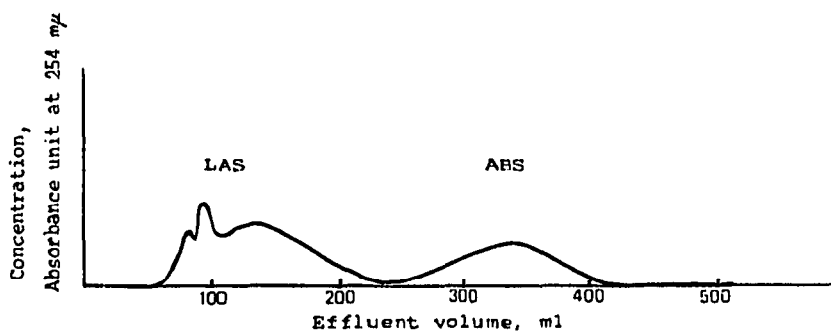The chromatogram is shown in Fig. 2. Two small peaks overlapping in front of

Fig. 2. Elution curve of a mixture of LAS and ABS. Column: 500 × 26 mm I.D.; resin: Amberlite CG-50 (100–200 mesh); eluent: 0.5 M $(NH_4)_2SO_4$–43% CH_3OH; flow rate: 0.45 ml/min; column temperature: 50°; weight of sample: 8.70 mg LAS, 9.20 mg ABS.

the LAS peak are assumed to be either due to the elution of by-products, such as disulfonate, or peaks based on the molecular weight distribution of LAS. Further investigation of these peaks was not carried out.

Peak resolution[18], which is the difference between the retention volumes of the two sulfonate peaks divided by the average value of the width of the two peaks, was more than unity.

Reproducibility and recovery

Recoveries of LAS and ABS from the column were each investigated independently in triplicate. Average recoveries of LAS and ABS were 93.4% and 99.2% respectively, and the reproducibility was satisfactory. The recoveries of LAS are

TABLE III

DETERMINATION OF EACH STANDARD SOLUTION AND KNOWN MIXTURES

Sample	Taken (mg)	Found (mg)	Recovery (%)	
LAS	7.90	7.35	93.1	
LAS	7.90	7.38	93.5	93.4
LAS	7.90	7.39	93.6	
ABS	8.80	8.73	99.2	
ABS	8.80	8.73	99.2	99.2
ABS	8.80	8.73	99.2	
LAS	8.70	8.74	100.5	
ABS	17.85	18.12	101.5	
LAS	17.40	17.41	100.1	
ABS	18.35	18.46	100.6	
LAS	17.40	16.96	97.5	
ABS	8.80	9.08	103.2	
LAS	26.10	25.38	97.3	
ABS	9.18	9.60	104.5	
LAS	25.50	24.60	96.3	
ABS	4.40	4.66	105.9	

somewhat lower and this may be due to by-products such as dialkylbenzene sulfonate contained in the sample. Accordingly, in case of the determination of LAS, a correction factor, 1.07, was used.

Known mixtures, prepared by mixing LAS and ABS in certain proportions, were analyzed and the results were shown in Table III.

From Table III, it appears that the agreement between the calculated and found values is satisfactory.

MECHANISM OF SEPARATION

It is thought that these surface active agents form micelles in aqueous solution, because the concentrations of both LAS and ABS used are only 10–20 mg/ml. In the case of a mixed sample, it is assumed that mixed micelles are formed at the first stage of
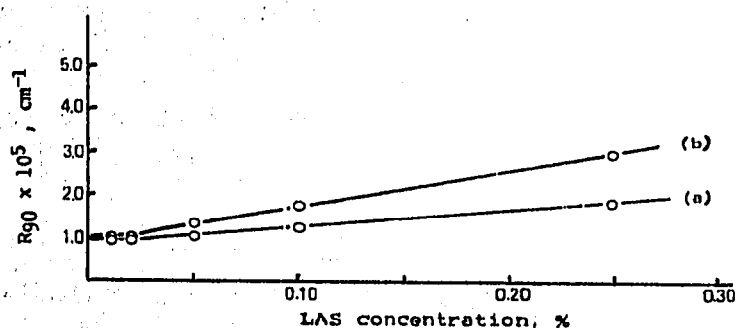

Fig. 3. Experimental Rayleigh ratios for solutions of LAS in 0.5 M ammonium sulphate–methanol. (a) 43% v/v methanol; (b) 35% v/v methanol.

sample addition. However, separation of LAS and ABS will not occur if the sample passes through the column in the form of mixed micelles. Therefore, it is presumed that the mixed micelles are each resolved to uni-molecules on addition of the eluent, and that LAS and ABS pass through the column in the state of uni-molecules.

PARFITT AND WOOD[10] examined the effect of methanol on micelle formation with respect to sodium dodecylsulfate in a methanol–water system. According to that paper, the micelles were not formed even though the sample concentration was increased and the molar fraction of methanol was more than 0.27 (about 40%).

In the present study, micelle formation in the eluent was investigated by a light scattering method. From Fig. 3, it appears that in an 0.5 M ammonium sulfate–43% methanol solution system micelles are not formed or only just begin to form. The inflexion point in Fig. 3 indicates micelle formation in 0.5 M ammonium sulfate–35% methanol solution system.

Accordingly, it was considered that the mixed sample was separated in the column in a uni-molecular state. When the concentration of alcohol in the eluent

TABLE IV

EFFECT OF CONCENTRATION OF METHANOL ON RECOVERIES OF LAS AND ABS

Sample taken: LAS 8.70 mg, ABS 9.20 mg. Concentration of ammonium sulfate: 0.5 M.

Concn. of methanol (%)	Recovery (%)	
	LAS	ABS
43	98.9	100.1
40	83.6	95.0
35	73.5	89.0

decreased, the recoveries of LAS and ABS also decreased as shown in Table IV. From these facts, it is apparent that the alcohol in the eluent plays an important role in the separation and determination of both sulfonates.

CONCLUSION

The mixture of LAS and ABS could be separated quantitatively by salting-out chromatography. From the point of view of molecular structure, LAS and ABS have only small differences in the alkyl chains which contribute to separate both sulfonates. This shows that the separation by salting-out chromatography is based on a delicate mechanism.

Further applications to the analysis of ionic surface active agent mixtures are being studied.

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